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Synthesis and physical properties of mono-estolides with varying chain lengths☆

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ABSTRACT

Saturated mono-estolide methyl esters and enriched saturated mono-estolide 2-EH esters were synthesized from oleic and different saturated fatty acids under three different synthetic routes. Estolide numbers (EN), the average number of fatty acid units added to a base fatty acid, varied with synthetic conditions. The attempts at obtaining saturated mono-estolide 2-EH esters, EN = 1, via distillation proved to be challenging, which lead to estolide samples with EN > 1 and the pour point values followed the same trend as the high EN estolides. The other synthetic routes provided saturated mono-estolide methyl esters with EN = 1. The resulting pour point values showed a linear relationship between the saturated capping chain length and pour point. As the saturated capping chain length increased the pour points also increased (higher temperatures): C-2 capped −30 °C, C-10 capped −12 °C, and C-18 capped 3 °C.

The saturated mono-estolide methyl ester viscosities also showed an increase in viscosity at 40 and 100 °C as the saturated chain lengths increased. The viscosities for the C-4 saturated mono-estolide methyl ester was 9.5 cSt at 40 °C and 2.6 cSt at 100 °C, while medium chain length derivations (C-10 saturated mono-estolide methyl ester) were 19.7 cSt at 40 °C and 4.2 cSt at 100 °C, and at the longer chain length derivations (C-18 mono-estolide methyl esters) were 27.6 cSt at 40 °C and 10.7 cSt at 100 °C. In general, a new series of saturated oleic mono-estolide methyl esters were synthesized and physical properties were collected. The physical property data indicated that both chain length and EN affect low temperature properties.

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1. Introduction

The use and investigation of bio-based industrial oils and derivatives have increased drastically in the past years. The U.S. has recently seen crude oil prices approaching $150/barrel compared to <$20/barrel in the late 1990s (www.zfacts.com). Past peaks in the crude oil markets have been followed by long periods of reduced prices, which have driven bio-based competitors out of the market. We are currently entering into the price range where bio-based materials are profitable but most companies and investors are concerned about the return of very low crude prices that history has shown (www.zfacts.com). Current data shows that increased prices are likely to continue as global demands increase and as the U.S. dollar weakens which will propel the demand for bio-based materials.

☆ Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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There has also been much debate on global warming and what is being done to the planet "Earth". The consumers of today are aware of their effects on the environment and are willing to replace petroleum products with bio-based "green" materials. These two recent world events have allowed and pressured researchers to explore bio-based materials as potential fuels, lubricants, and base material for industrial products. In particular, the basic questions such as "What makes a bio-based material a good lubricant?" or "How does structure impact certain physical properties?" are now being investigated and reported in the literature (Cermak et al., 2007b).

Estolides are one example of a bio-based material that will help lessen our demand on foreign oils as well as limit our greenhouse emissions. Estolides have been found in nature (Plattner et al., 1979) and have been synthesized (Isbell et al., 1994, 2000b; Cermak and Isbell, 2000) in the laboratory which has led to the development of new products from industrial new crops (Cermak and Isbell, 2000, 2001a,b; Isbell et al., 2000a).

Estolides are a class of esters, based on vegetable oils (Isbell et al., 1994, 2000b), made by the formation of a carbocation at the site of unsaturation that can undergo nucleophilic addition by another fatty acid, with or without carbocation migration along the length of the chain, to form an ester linkage. These linkages are used to help characterize the structure of the estolide since the estolide number (EN) is defined as the average number of fatty acids added to a base fatty acid (Fig. 1, $EN = n + 1$). The secondary ester linkages of the estolide are more resistant to hydrolysis than those of triglycerides, and the unique structure of the estolide results in materials that have far superior physical properties for certain applications than vegetable and mineral oils (Cermak and Isbell, 2002).

Estolides were developed to overcome some of the short falls associated with vegetable oils which are known to have poor thermal oxidative stability (Becker and Knorr, 1996; Cermak and Isbell, 2003a) and poor low temperature properties (Asadauskas and Erhan, 1999). Some of these deficiencies can be improved with the use of additive packages, but usually at the sacrifice of biodegradability, toxicity, and cost.

In the early 2000s Cermak and Isbell (2001b, 2002) developed a series of saturated estolides in which oleic acid and saturated fatty acids ranging from butyric through stearic were treated with 0.4 equiv. of perchloric acid at either 45 or 55 °C to produce complex estolides, saturated-oleic estolide 2-ethylhexyl (EH) esters (Fig. 1). Yields varied between 45 and 65% after Kugelrohr distillation. The EN varied with reaction temperature as well as with the change in saturated fatty acids. The shorter-chain, saturated fatty acids, i.e. butyric and hexanoic acid, provide material with higher degrees of oligomerization ($EN = 3.3$) than stearic acid ($EN = 1.4$). These saturated estolides and estolide esters showed very different physical properties in terms of cold temperature properties. Cermak and Isbell (2002) theorized that by varying the capping material on the estolide the crystal lattice structure of the material was disrupted as it approached its pour point, which lead to estolide esters with excellent low temperature properties, pour points of −36 °C and cloud points of −41 °C. These saturated-capped estolide 2-ethylhexyl esters thus have eliminated common problems associated with the use of vegetable oils as functional fluids.

All estolides and estolide esters to date from oleic acid, saturates, meadowfoam (Isbell and Kleiman, 1996), tallow (Cermak et al., 2007b), castor and lesquerella oil (Isbell and Cermak, 2002), or any source of hydroxy fatty acids (Zerkowski and Solaiman, 2007) have shown promise as either cosmetics, coatings, or biodegradable lubricants. These estolides and esters usually out-perform the commercially available industrial products such as petroleum-based hydraulic fluids, soy-based fluids, and petroleum oils (Cermak and Isbell, 2003b).

In this paper, we report the synthesis and physical properties from saturated mono-estolide of methyl and 2-ethylhexyl

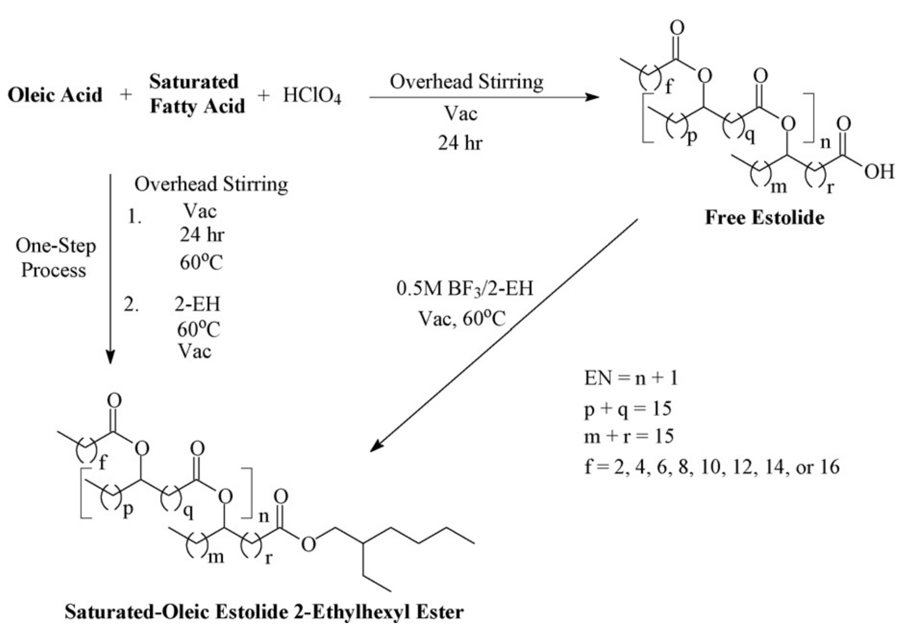

Fig. 1 – Acid-catalyzed condensation reaction scheme for the formation of saturated-oleic estolide esters.

esters. The physical properties of the mono-estolide esters were compared to previously synthesized high EN saturated capped estolides. Correlations between EN and low temperature properties were explored.

2. Materials and methods

2.1. *Materials*

Oleic acid (90%), acetic anhydride (>98%), butyric anhydride (98%), perchloric acid (70%), tin(II) 2-ethylhexanoate (95%), pyridine (≥99.0), and hexanoic acid (99%) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Ethyl acetate, hexanes, acetone, butyric acid (99+%), octanoic acid (99%), sodium hydroxide (≥98), palmitic acid (95%), concentrated sulfuric acid (98%), methanol, and 2-ethylhexyl alcohol were purchased from Fisher Scientific Co. (Fairlawn, NJ). Decanoic acid (99%), myristic acid (97%), lauric acid (97%), and stearic acid (95%) were purchased from Pfaltz & Bauer Inc. (Waterbury, CT). Potassium hydroxide was obtained from J.T. Baker Chemical Co. (Phillipsburg, NJ). Filter paper was obtained from Whatman (Clifton, NJ). Acetonitrile and acetic acid (both for high-performance liquid chromatography (HPLC)) were obtained from EM Science (Gibbstown, NJ). Ethanol was purchased from AAPER Alcohol and Chemical Company (Shelbyville, KY). Acetonitrile and acetic acid (both for HPLC), charcoal, sodium hydrogenphosphate, and sodium dihydrogenphosphate were obtained from EM Science (Gibbstown, NJ). The fatty acid methyl ester (FAME) standard mixtures were obtained from Alltech Associates, Inc. (Deerfield, IL). Solvents for chromatography and extraction were HPLC grade or an equivalent, and were used without further purification.

2.2. *Equipment and procedures*

2.2.1. *Gas chromatography (GC)*

This analysis was performed with a Hewlett-Packard 5890 Series II gas chromatograph (Palo Alto, CA), equipped with a flame-ionization detector and an autosampler/injector. Analyses were conducted on a SP-2380 30 m × 0.25 mm i.d. column (Supelco, Bellefonte, PA). Saturated C_8–C_{30} FAMEs provided standards for making fatty acid and by-product assignments.

Parameters for SP-2380 analysis were column flow 1.4 ml/min with helium head pressure of 136 kPa; split ratio 50:1; programmed ramp 120–135 °C at 10 °C/min, 135–175 °C at 3 °C/min, 175–265 °C at 10 °C/min, hold 5 min at 265 °C; injector and detector temperatures set at 250 °C. Retention times for eluted peaks were methyl hexanoate 2.4 min, methyl octanoate 3.0 min, methyl decanoate 4.2 min, methyl laurate 4.2 min, methyl myristate 6.1 min, methyl palmitate 8.8 min, methyl stearate 12.2 min, and methyl oleate 13.1 min hydroxy compounds.

2.2.2. *GC–mass spectrometry (GC–MS)*

GC–MS was performed on a Hewlett-Packard 5890A GC with a 30 m × 0.20 mm i.d. SPB-1 column (Supelco, Bellefonte, PA) and a Hewlett-Packard 5970 mass selective detector. GC conditions: helium head pressure 15 psi (103 kPa) at 170 °C set for constant flow with varying pressure; split ratio 50:1; injector temperature set at 250 °C; transfer line temperature set at 250 °C; programmed ramp from 170 to 270 °C at 3 °C/min. MS conditions: mass range 50–550 amu; electron multiplier 200 V relative.

2.2.3. *High-performance liquid chromatography*

Reverse-phase HPLC analyses were performed on a Thermo Separations Spectra System AS1000 autosampler/injector (Fremont, CA) with a P2000 binary gradient pump from Thermo Separation Products (Fremont, CA) coupled to a Alltech ELSD 500 evaporative light scattering detector (Alltech Associates, Deerfield, IL). A C-8 reverse-phase analysis used to separate reaction mixtures was carried out with a Dynamax column (250 mm × 4.5 mm, 8 μm particle size) from Rainin Instrument Co. (Woburn, MA). A 16-min run time was used to follow the reaction, which provided information on the overall progress of the reaction. The flow rate of 1 ml/min; 0–4 min 80% acetonitrile, 20% acetone; 6–10 min 100% acetone; 11–16 min 80% acetonitrile, 20% acetone. The ELSD drift tube was set at 55 °C with the nebulizer set at 20 psi (138 kPa) N_2, providing a flow rate of 2.0 standard liters per minute (SLPM). Retention times for eluted peaks: estolides, 10.3–13.9 min; oleic acid, 5.8 min, and methyl hydroxy stearate, 4.7 min.

2.2.4. *Estolide number*

Estolide numbers were either determined by GC from the SP-2380 column analysis as described previously by Isbell and Kleiman (1994) or by nuclear magnetic resonance (NMR) analysis by assigning the integration, of the methoxy (–OCH_3) signal to three or the methylene (—CH_2—OC(O)—) signal to two, and recording the integration of the estolide signal (CH—O—(C=O)—CH_2—) as the estolide number.

2.2.5. *GC analysis of hydroxy fatty acids*

Analytical estolide samples for GC were prepared using procedures described by Cermak and Isbell (2001b).

2.2.6. *TMS derivatization of hydroxy fatty esters*

Analytical estolide samples for GC were prepared using procedures described by Cermak and Isbell (2001b).

2.2.7. *Gardner color*

Lovibond 3-Field Comparator from Tintometer Ltd. (Salisbury, England) using AOCS method Td 1a-64 (Firestone, 1994b) was used for Gardner color measurements. Gardner color of both the residue and distillate materials was measured throughout the distillation. The "+" and "−" notation was employed to designate samples that did not match one particular color.

2.2.8. *Viscosity and viscosity index*

Calibrated Cannon-Fenske viscometer tubes obtained from Cannon Instrument Co. (State College, PA) were used to measure viscosity. Measurements were run in a Temp-Trol (Precision Scientific, Chicago, IL) viscometer bath set at 40.0 and 100.0 °C. Viscosity and viscosity index were calculated using ASTM methods D 445-97 (ASTM, 1997) and ASTM D 2270-93 (ASTM, 1998), respectively. Duplicate measurements were made and the average values were reported.

2.2.9. Pour point (PP)

ASTM method D97-96a (ASTM, 1996) was used to measure pour points to an accuracy of ±3 °C. The pour points were determined by placing a test jar with 50 ml of the sample into a cylinder submerged in a cooling medium. The sample temperature was measured in 3 °C increments at the top of the sample until the material stopped pouring. This point is determined when the material in the test jar did not flow when held in a horizontal position for 5 s. The temperature of the cooling medium was chosen based on the expected pour point of the material. Samples with pour points that ranged from +9 to −6, −6 to −24, and −24 to −42 °C were placed in baths of temperature (−18, −33, and −51 °C), respectively. The pour point was defined as the coldest temperature at which the sample still poured. All pour points were run in duplicate and average values were reported.

2.2.10. Cloud point (CP)

ASTM method D 2500-99 (ASTM, 1999) was used to measure cloud points to an accuracy of ±1 °C. The cloud points were determined by placing a test jar with 50 ml of the sample into a cylinder submerged into a cooling medium. The sample temperature was measured in 1 °C increment at the bottom of the sample until any cloudiness was observed at the bottom of the test jar. The temperature of the cooling medium was chosen based on the expected cloud point of the material. Samples with cloud points that ranged from room temperature to 10, 9 to −6, and −6 to −24, −24 to −42 °C were placed in baths of temperature (0, −18, −33, and −51 °C), respectively. The cloud point was defined as the coldest temperature at which the sample remained opaque. All cloud points were run in duplicate and average values were reported.

2.2.11. Acid value

751 GPD Titrino from Metrohm Ltd. (Herisau, Switzerland) was used for measurements. Acid values were determined by the official AOCS Method (Firestone, 1994a) with ethanol substituted for methanol to increase the solubility of the estolide ester during the titration. All acid values were run in duplicate and average values were reported.

2.2.12. General synthesis and distillation of mono-estolide 2-ethylhexyl esters

An acid-catalyzed condensation reaction was conducted without solvent in a 2000-ml jacketed reactor with a three-necked reaction kettle cover that had been pre-treated with an acidic wash. Oleic acid (500.0 g, 1770 mmol) and lauric fatty acid (354.8 g, 1770 mmol) were combined together and heated to 60 °C under house vacuum. Once the desired temperature of 60 ± 0.1 °C was reached, perchloric acid (177 mmol, 15.3 ml, 0.1 equiv.) was added and the flask was placed under vacuum and stirred with a Teflon stir bar on a stir plate. After 24 h, 2-ethylhexyl alcohol (666.4 g, 4.621 mol, 800.0 ml) was added to the vessel, vacuum was restored, and the mixture was stirred for an additional 3–4 h to yield the estolides reported in Table 1. The completed reactions were quenched by the addition of KOH (11.9 g, 212 mmol, 1.2 equiv. based on $HClO_4$) in 90% ethanol/water (50 ml) solution. The solution was allowed to cool with stirring for 45 min followed by filtration through a Buchner funnel with Whatman #1 filter paper. The organic layer was dried over sodium sulfate and filtered through a Buchner funnel with Whatman #1 filter paper. All reactions were concentrated *in vacuo* then Kugelrohr-distilled at 90–110 °C at 6–13 Pa to remove any excess ethanol and 2-ethylhexyl alcohol. The residue was Kugelrohr-distilled at 180–200 °C at 6–13 Pa to remove any unreacted saturated and unsaturated fatty acids and by-products (Cermak and Isbell, 2001b). The yields of the reactions varied from 60 to 78% depending on stirring and house vacuum conditions. Estolide numbers were determined by GC as described above and ranged from 3.3 to 1.4.

The residual capped estolide 2-ethylhexyl esters from the Kugelrohr-distillation underwent further distillation in attempt to isolate a mono-estolide, EN = 1. The distillation of estolide esters into mono-estolide esters versus higher molecular weight poly-estolide esters was conducted on a Myers Lab 3 (Cermak et al., 2007a) short-path molecular distillation unit (Myers Vacuum, Kittanning, PA) from the remaining residual capped estolide 2-ethylhexyl esters from the Kugelrohr-distillation. The feedstock was metered onto a heated rotor spinning at 28.75 Hz, cold tap water was used to cool the diffusion pump and rotor bearing, and placed under a high vacuum (0.08–0.40 Pa) at both the chamber and fore-line pressure sensors. Once on the hot spinning surface, a thin film was formed where rapid heat transfer occurred, thus promoting distillation of the lower molecular weight estolide esters from the higher weight fatty acids. The material that remained undistilled flowed rapidly off the rotor into the residue flask, which was maintained under vacuum at room

Table 1 – Physical properties of saturated mono-estolide 2-ethylhexyl esters[a]

Estolide	Capped length	Pour point (°C)	Cloud point (°C)	Vis at 40 °C (cSt)	Vis at 100 °C (cSt)	Viscosity index	Gardner color
A	4	−30	<−30	51.3	9.4	169	4−
B	6	−30	−30	56.5	9.9	163	6−
C	8	−42	−35	40.0	7.8	169	4−
D	10	−42	−30	32.0	6.8	179	2
E	12	−30	−20	37.9	7.5	170	2−
F	14	−21	−13	34.7	7.1	173	2
G	16	−15	0	45.2	8.3	161	2+
H	18	0	12	46.1	9.5	195	3

[a] Reactions were run for 24 h with overhead stirring under vacuum, with 0.1 equiv. of perchloric acid at 60 °C, then excess amounts of 2-ethylhexanol at 60 °C for 3–4 h followed by distillations at 90–110 °C and 180–200 °C followed by molecular distillation.

temperature. This short residence time at high temperature helped to reduce degradation and color bodies of the residue unlike other distillations where the sample remains at the distillation temperature for several hours. The distillate fraction was collected on the front condenser plate, which was cooled with tempered water (~40 °C). The distillate exited the chamber and flowed into the distillate flask, which was also maintained under vacuum and at room temperature. Estolide numbers were determined by NMR as described above and ranged from 1.4 to 0.9.

2.2.13. *General synthesis of hydroxy methyl stearate esters*

An acid-catalyzed condensation reaction was conducted without solvent in a 3000 ml jacketed reactor with a three-necked reaction kettle cover that had been pre-treated with an acidic wash. To oleic acid (500.0 g, 1.773 mol) was added perchloric acid (1.773 mol, 153.4 ml, 1.0 equiv.) at which time the flask was placed under vacuum and stirred with a Teflon stir bar on a stir plate. After 24 h, methanol (1186 g, 37.06 mol, 1500 ml) was added to the vessel, addition of a water-cooled condenser and the solution was heated to reflux for 36 h. The completed reactions were quenched by the addition of NaOH (6.38 g, 159.6 mmol, 0.9 equiv. based on $HClO_4$) in 90% methanol/water (100 ml) solution. The solution was allowed to cool with stirring for 45 min followed by transfer to a separatory funnel. Addition of hexane 2000 ml followed by the organic layer being washed with NaH_2PO_4, pH 5 buffer (3× 250 ml) or until the pH was ~5 by pH paper. The organic layer was dried over sodium sulfate and filtered through a Buchner funnel with Whatman #1 filter paper. The reaction was concentrated *in vacuo* to provide a solid product. The isolated product was recrystallized, the solid product had hexane added in a 2.75:1.00 hexane to hydroxyl containing material. The solution was heated on a steam bath until all the solids were dissolved, the material was allowed to cool to RT, followed by 1 h at 0 °C, and finally cooled to −25 °C for 23 h. The crystals were collected via vacuum filtration through a Buchner funnel with Whatman #1 filter paper. The collected crystals were washed with hexane (250 ml) at −25 °C. The crystals were concentrated *in vacuo* followed by Kugelrohr-distillation at 180–200 °C at 6–13 Pa to remove color bodies and estolide by-products. The yield of pure isolated hydroxy methyl stearate ester was about 40%.

2.2.14. *General synthesis of mono-estolide methyl esters C2–C4*

Synthesis of short chain capped estolides were conducted in a three-necked round bottom flask equipped with magnetic stirrer, cold water condenser, and a heating mantle controlled by a J-Kem Gemini-2 (St. Louis, MO) temperature controller utilizing a temperature probe. Hydroxy methyl stearate ester (50.0 g, 159 mmol) was combined with acetic anhydride (40.6 g, 398 mmol). Pyridine (2.36 g, 29.9 mmol) was added as a catalyst and the mixture was heated to 50 °C for 24 h then dissolved in hexane (300 ml) and washed with 5% H_2SO_4 (aq) (3× 150 ml), brine (3× 150 ml), and NaH_2PO_4 (pH 5 buffer) (3× 150 ml) solution. Butyric anhydride reactions were conducted at 60 °C for 6 h then dissolved in hexane (300 ml) and washed with 1 M KOH (3× 150 ml), saturated brine (3× 150 ml), NaH_2PO_4 (pH 5 buffer) (3× 150 ml), Na_2HPO_4 (pH 9 buffer) (3× 150 ml). Ethanol was added to break the emulsions. The organic layer was dried over sodium sulfate and filtered through a Buchner funnel with Whatman #1 filter paper. All reactions were concentrated *in vacuo* then Kugelrohr-distilled at 180–200 °C at 6–13 Pa the residue was collected as shorter chain mono-estolide methyl esters. Estolide numbers were determined by NMR as described above and were ranged from 1.0 to 0.9.

2.2.15. *General synthesis mono-estolide methyl esters C6–C18*

Synthesis of long chain-capped estolides was conducted without solvent in a 1000-ml three-necked flask which was fitted with a temperature probe, vacuum adapter, and a stopper. To hydroxy methyl stearate ester (65.0 g, 207 mmol) was added octanoic acid (119 g, 828 mmol, 4.0 equiv.) and tin(II) 2-ethylhexanoate (1.84 g, 4.54 mmol, 1% wt of acids) at which time the flask was placed under vacuum (~10 Torr) while magnetically stirred. The reactions were heated to 130 °C using a heating mantle controlled by a J-Kem Gemini-2 (St. Louis, MO) temperature controller utilizing a temperature probe immersed below the liquid level in the flask as well as two condensers connected in series (this condenser setup was necessary to recirculate all the unreacted fatty acids back into the flask). The first condenser was connected to a recirculating water bath and maintained at a temperature slightly above the melting point of the fatty acid. The second condenser was connected to the first with a distilling head and cooled with cold tap water. The outlet of the second condenser was fitted with a vacuum distillation adapter and round bottom flask to collect the water of reaction. After 24 h, the solution cooled to room temperature under vacuum. The material had 2% charcoal added and allowed to stir at RT for 3 h followed by vacuum filtration through a Buchner funnel with Whatman #1 filter paper. The remaining material was subjected to Kugelrohr-distillation at 180–200 °C at 6–13 Pa and the residue was collected as longer chain mono-estolide methyl esters. The yields of the reactions varied from 60 to 87% depending on stirring and house vacuum conditions. Estolide numbers were determined by NMR as described above and were ranged from 1.2 to 0.9.

2.2.16. *Nuclear magnetic resonance*

All NMR spectra were collected on a Bruker Avance 500 (Billerica, MA) spectrometer with a 5-mm BBI probe. All spectra were acquired at 300.0 K using $CDCl_3$ as a solvent in all experiments. Chemical shifts are reported as parts per million from tetramethylsilane with an absolute frequency 500.11 MHz. The assignments of protons were not to the whole number. The representative NMR sample contained a compound that had an average estolide number of 1.24 for the estolide ester (C, Table 1) and 1.00 for the estolide ester (L, Table 2) which made whole number assignment difficult. The data reported for the number of protons in the NMR reflected the actual numbers.

2.2.16.1. *^{1}H and ^{13}C NMR of 2-ethylhexyl 9-(octanoyloxy) octadecanoate ester C (Table 1).* ^{1}H NMR: δ 5.38–5.36 (*m*, 0.64H, —CH=CH—), 4.88–4.85 (*m*, 1.24H,—CH—O—(C=O)—CH_2—), 3.98 (*d*, *J* = 6.0 Hz, 2.0H, —O—CH_2—CH(CH_2—)CH_2—), 2.30–2.25 (*m*, 4.7H, —CH_2—(C=O)—O—CH_2—, —CH_2(C=O)—O—CH—), 1.96–1.26 (*m*, 58.7H), and 0.91–0.86 ppm (*m*, 13.3 H, —CH_3). ^{13}C NMR: δ 173.9 (*s*, C=O), 173.9 (*s*, C=O), 74.0 (*d*, —CH—O—C=O), 66.5 (*t*,

Table 2 – Physical properties of saturated mono-estolide methyl esters[a]

Estolide	Capped length	Pour point (°C)	Cloud point (°C)	Vis at 40 °C (cSt)	Vis at 100 °C (cSt)	Viscosity index	Gardner color
I	2	−30	−3	9.5	2.6	117	1−
J	4	−27	−12	9.6	2.7	134	1−
K	6	−21	10	10.4	2.9	151	1
L	8	−24	−3	12.3	4.0	258	1−
M	10	−12	0	19.7	4.2	121	5+
N	12	−12	−3	20.0	4.1	101	1−
O	14	−15	−3	20.3	5.3	218	7+
P	16	−3	6	22.2	5.2	178	2+
Q	18	3	12	27.6	10.7	407	3+

[a] Reactions I and J were synthesized via anhydrides and the other estolides via tin and the corresponding fatty acid under condition listed in Section 2.

—O—CH_2—CH—), 38.6 (*d*, —CH_2—CH(CH_2—)—CH_2—), 34.6 (t), 34.3 (t), 34.3 (t), 34.3(t), 32.5 (t), 31.8 (t), 31.8 (t), 31.7 (t), 31.2 (t), 30.3 (t), 29.5 (t), 29.4 (t), 29.3 (t), 29.2 (t), 29.1 (t), 29.0 (t), 28.8 (t), 25.2 (t), 25.1 (t), 24.9 (t), 24.8 (t), 24.7 (t), 23.7 (t), 22.9 (t), 22.6 (t), 22.2(t), 14.0 (*q*, —CH_3), 13.9 (*q*, —CH_3), 13.8 (*q*, —CH_3), and 10.9 ppm (*q*, —CH_3).

2.2.16.2. *^{1}H and ^{13}C NMR of methyl 9-(octanoyloxy) octadecanoate ester L (Table 2)*. ^{1}H NMR: δ 4.89–4.86 (*m*, 1.0H,—*CH*—O—(C=O)—CH_2—), 3.68 (*s*, 3.0H, —O—*CH_3*), 2.33–2.29 (*m*, 4.1H, —*CH_2*—(C=O)—O—CH_2—, —*CH_2*(C=O)—O—CH_3), 1.65–1.29 (*m*, 40.0H), and 0.91–0.86 ppm (*t*, *J* = 7.5 Hz, 6.3H, —*CH_3*). ^{13}C NMR: δ 174.2 (*s*, C=O), 173.6 (*s*, C=O), 73.9 (*d*, —CH—O—C=O), 51.4 (*q*, —O—CH_3), 34.7 (t), 34.1 (t), 34.1 (t), 34.0 (t), 34.0 (t), 34.0 (t), 33.9 (t), 33.9 (t), 31.9 (t), 31.7 (t), 31.7 (t), 28.9 (t), 28.9 (t), 28.9 (t), 28.9 (t), 28.9 (t), 24.9 (t), 24.9 (t), 24.9 (t), 24.8 (t), 24.8 (t), 22.7 (t), 22.6 (t), 22.6 (t), 14.1 (*q*, —CH_3), and 14.0 ppm (*q*, —CH_3).

3. Results and discussion

Table 1 outlines a series of estolides (Fig. 1) with different “capped” saturated fatty acids. The reaction conditions had previously been reported by Cermak and Isbell (2001b) but the physical properties were based on what the reaction produced (Cermak and Isbell, 2001a). Estolides are formed from the cationic homo-oligomerization of unsaturated fatty acids resulting from the addition of a fatty acid carboxyl adding across the olefin (Isbell et al., 1994). This condensation can continue, resulting in oligomeric compounds where the average extent of oligomerization is defined as the estolide number (EN = n + 1, Fig. 1) (Isbell and Kleiman, 1994). When saturated fatty acids are added to the reaction mixture, the oligomerization terminates upon addition of the saturated fatty acid to the olefin since the saturate provides no additional reaction site to further the oligomerization. Consequently, the estolide is stopped at this point from further growth, thus we term the estolide as being “capped” (Cermak and Isbell, 2001b). The estolide physical properties reported in the past (Cermak and Isbell, 2002) had estolide numbers, EN, that ranged from 3.3 to 1.4. The effects of EN on the cold temperature properties was of particular interest.

Cermak and Isbell (2001b) showed that complex estolides had the best low temperature properties when capped with mixtures of very short chains, saturated fatty acids such as those present in cuphea and coco (Cermak and Isbell, 2001a, 2003b). Individual pure fatty acids like decanoic acid had the best cold temperature properties, with a pour point of −39 °C, which was followed by octanoic and lauric acids.

In this paper we synthesized mono-estolides, EN = 1, and examined their physical properties, in particular cold temperature. Initially oleic acid was combined with different saturated fatty acids with catalytic amounts of perchloric as shown in Table 1. The acid-catalyzed process converted the fatty acids to the free acid estolides under vacuum at 60 °C followed by an *in situ* esterification with 2-ethylhexyl alcohol under similar conditions. The final products underwent vacuum distillation to remove any excess fatty acids, fatty esters, by-products, and 2-ethylhexyl alcohol, providing neat estolide ester samples. The EN of the estolides were greater than 1 as determined by GC. Therefore, the estolides had to be separated into mono-estolides and poly-estolides fractions via a short-path vacuum distillation. The short-path vacuum distillation apparatus has proven useful in the separation of meadowfoam estolides (Isbell and Cermak, 2004) and cuphea fatty acids (Cermak et al., 2007a). The saturated-oleic estolide esters were distilled using this method in an attempt to produce an estolide with an EN = 1. The NMR analysis showed that the EN was not all equal to 1 but had dramatically been reduced as shown in Table 1. The distilled materials were characterized as the saturated mono-oleic estolide 2-ethylhexyl esters (i.e. C-10 as 2-ethylhexyl 9-(decanoyloxy)octadecanoate ester) and the physical properties were recorded in Table 1.

Of particular interest were the cold temperature properties of the saturated mono-estolide 2-EH esters highlighted in Fig. 2. The same general trend was observed with the saturated mono-estolide 2-EH esters case that Cermak and Isbell (2002) reported in 2002. The pour point data suggests that the C8 and C10 should produce 2-EH estolide esters that have the best pour points while the others fatty acids had higher pour points to produce a bell-shaped curve.

The question at this point became, was the improved low temperature properties of the saturated mid-chain capped estolides a function of EN or structure of the estolide esters. It was theorized that the C-8 and C-10 had nothing unusual, as compared to the other saturated capping materials, to lend to the depressed pour points, thus this depression must be a function of the EN. Therefore, an estolide ester had to be

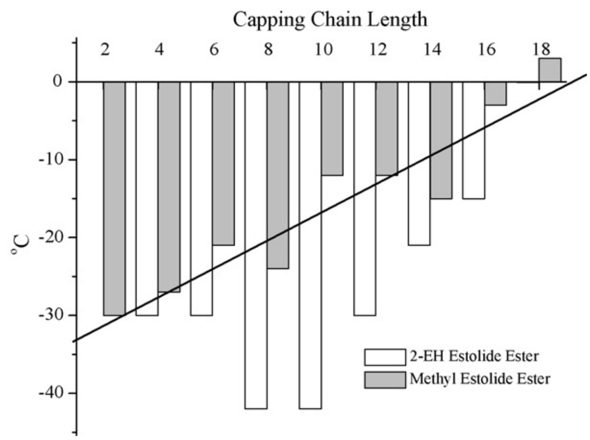

Fig. 2 – Effect of estolide fatty acid capping group on pour point.

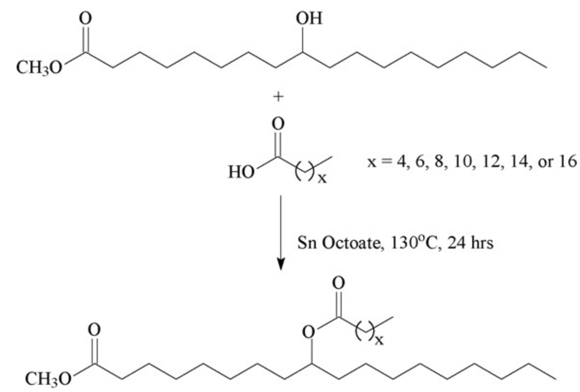

Fig. 4 – General synthesis of mono-estolide methyl esters C6–C18.

produced with an EN = 1 in order to test this theory. The most practical method to obtain a saturated mono-estolide ester became a synthesis project where the EN could be controlled and the physical properties could be measured accurately.

The synthetic approach to produce a saturated mono-estolide ester began with an acid-catalyzed conversion of oleic acid and perchloric acid to produce an estolide as above but methanol, instead of 2-EH alcohol, was added and allowed to react for longer periods of time than the normal time usually associated with the esterification process. Under such conditions, the estolide was broken down into hydroxy methyl stearate esters and methyl stearate esters. The mixture underwent a recrystallization process with hexane to isolate the hydroxy methyl stearate esters. The methyl hydroxyl stearate esters were used as the base unit for the synthesis of the saturated mono-estolide methyl esters.

The hydroxy methyl stearate esters were envisioned undergoing an esterification reaction with excess amounts of longer chain saturated fatty acids in the presence of tin reagent as demonstrated in Fig. 3. This method proved to be a very useful synthetic technique in the synthesis of lesquerella and castor oil estolides (Isbell et al., 2006). A range of saturated fatty acids were subjected to the esterifications but only the C-6 to C-18 fatty acids produced saturated mono-estolide methyl

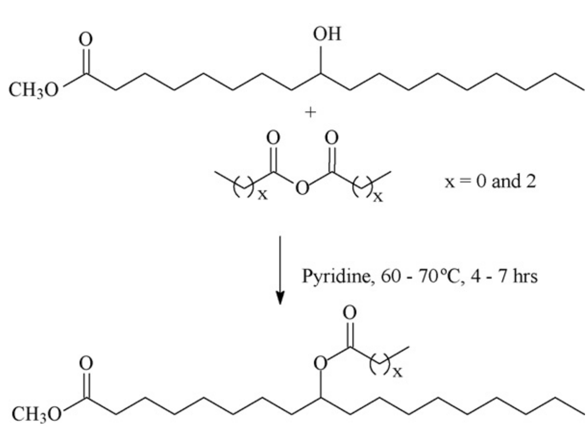

Fig. 3 – General synthesis of mono-estolide methyl esters C2–C4.

esters. Under the reaction conditions described, the very short saturated fatty acids, C-2 and C-4, could not survive the reaction conditions and were lost through the vacuum due to the volatility of these short chains. The shorter saturated capped mono-estolide methyl esters were produced with the hydroxy methyl stearate esters that were subjected to acid anhydride conditions to produce the shorter saturated mono-estolides methyl esters demonstrated in Fig. 4.

In all cases, the EN of the saturated mono-estolide esters from both synthetic pathways was much closer to an EN value of 1. The synthetic approach was a superior method at producing a saturated mono-estolide ester versus the distillation approach that had some potential difficulties. The physical properties, i.e. pour points, for the saturated mono-estolide esters are shown in Fig. 2. The darkened line plots a linear relationship ($R^2 = 0.946$) for the pour points. Pour points increase as the saturated fatty acid capping material increases in chain-length for the saturated mono-estolide methyl esters. The butyric, C-4, capped material had the best pour point at −30 °C while the stearic, C-18, capped material had pour points greater than 0 °C. The linear relationship of the methyl esters was not observed with the 2-EH ester series which showed a bell-shaped curve. This curve shape was also observed with the high EN saturated estolide 2-ethylhexyl esters.

The viscosities of the saturated mono-estolide methyl esters, Table 2, increased as the saturated chain lengths increased. The viscosities for the C-4 saturated mono-estolide methyl ester was 9.5 cSt at 40 °C and 2.6 cSt at 100 °C, while medium chain length derivations (C-10 saturated mono-estolide methyl ester) were 19.7 cSt at 40 °C and 4.2 cSt at 100 °C, and at the longer chain length derivations (C-18 mono-estolide methyl esters) was 27.6 cSt at 40 °C and 10.7 cSt at 100 °C.

The Gardner colors in all the entries, Tables 1 and 2, were in general very light. The colors would be suitable for a bio-lubricant and compares with current materials in the market. Table 1 entries were lighter in color after distillation versus the starting color of the high EN estolides. The short-path vacuum distillation did an outstanding job at removing color bodies by not superheating either the residue or the distillate fractions which was consistent with past distillation studies (Isbell and Cermak, 2004).

The proton NMR for the saturated mono-estolide 2-EH esters in Table 1, specifically the octanoic mono-estolide 2-EH ester C, shows the key features of the typical estolide 2-EH esters. The ester methine signal at 4.88–4.85 ppm is indicative of an estolide linkage. Another distinctive feature is the multiplet α-methylene proton shift (2.30–2.25 ppm) adjacent to the two esters. The NMR indicates the presence of alkene in the estolide by the appearance of a small alkene signal at 5.38–5.36 ppm. The alkene signal indicated that some of the estolide was capped with unsaturated material, i.e. oleic acid, which is common with estolides synthesized under these conditions.

The carbon NMR spectrum contains the expected estolide 2-EH ester signals. There are three different carbonyl signals present in the 173-ppm region (estolide carbonyl and 2-EH ester carbonyl). The lack of the shift in the 179-ppm region indicates the estolides have been converted to the 2-EH ester which supports the acid value numbers in Table 1. The other distinctive signal was the methine carbon, estolide signal, at 73.9 ppm, which is common to all estolides. The signal at 66.5 ppm is characteristic to the 2-EH ester methylene functionality adjacent to the ester. These major peaks in the carbon NMR were also confirmed by a DEPT experiment.

The proton NMR for the saturated mono-estolide methyl esters in Table 2, specifically the octanoic mono-estolide methyl ester L, shows the same key features of the typical estolide 2-EH esters from Table 1, except that the estolide methyl ester had a methylene doublet at 3.96 ppm which was replaced with a singlet at 3.68 ppm from the methyl ester. The spectrum also did not contain any alkene signals which was different than the estolides in Table 1. The carbon NMR spectra contained the expected estolide methyl ester signals at 73.9 ppm while only having just two different carbonyl signals present in the 173-ppm region (estolide carbonyl and methyl ester carbonyl). Finally, the methyl ester signal at 51.4 ppm was a distinctive indication of the ester being present. These major peaks in the carbon NMR were also confirmed by a DEPT experiment.

Methyl 9-(decanoyloxy)octadecanoate ester M (Table 2) was saponified with 0.5 M KOH/MeOH then esterified with 1 M H_2SO_4/MeOH to give the corresponding hydroxy and non-hydroxylated fatty esters. The isolated mixture of fatty acid esters was then silylated and analysed by GC–MS (Erhan and Kleiman, 1992). The main mass spectral features were *m/e* 371 (M+ −15, 2.53%), 73 (TMS+, 100%), and a Gaussian fragment curve representing cleavage at the C—C bond adjacent to the silyloxy positions (masses 173–315). The fragments and abundances were very similar to previously reported complex saturated estolide data (Cermak and Isbell, 2001b). The estolide position was distributed from positions 5–13 (Table 3) with the original Δ9 and Δ10 positions having the largest abundances in the mass spectrum, which also was very similar to previously reported complex estolide data (Cermak and Isbell, 2001b). This method demonstrated that during the estolide reaction there was migration. This complex mixture was carried into the formation of the hydroxy methyl stearate ester and onto the saturated mono-estolides methyl esters. This same Gaussian curve was also observed in the estolide esters reported in Table 1.

Table 3 – Estolide position as determined by gas chromatography–mass spectrometry (GC–MS) of trimethylsilyl ether of alkali-hydrolyzed estolide M (Table 2)[a]

Hydroxy position	MS fragments		Total abundance
	Carbonyl	Alkyl	
5	203	285	1
6	217	271	3
7	231	257	9
8	245	243	21
9	259	229	61
10	273	215	61
11	287	201	21
12	301	187	2
13	315	173	1

[a] The same relative results were obtained for all mono-estolides.

4. Conclusions

Saturated mono-estolide methyl esters and enriched saturated mono-estolide 2-EH esters have been synthesized from oleic and different saturated fatty acids under three different synthetic routes. The resulting pour points and other physical properties of the saturated mono-estolide 2-EH esters followed the same general trend that the high EN estolide samples generally follow. This led to the saturated mono-estolide methyl ester series that had EN = 1 in all cases. The pour points of this series followed a linear trend, as the chain length increased the pour points increased (increase in temperatures) which was a completely different trends than the enriched saturated mono-estolide 2-EH ester pour points that resembled a bell-shaped curve. The saturated mono-estolide methyl ester viscosities also showed an increase in viscosity at 40 and 100 °C as the saturated chain lengths increased. In general, a new series of saturated oleic mono-estolide methyl esters were synthesized and physical properties collected to prove that chain length and EN both affect low temperature properties.

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